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In reapplication of: Paul Bruinsma, Suresh Baskaran, Jagannadha R. Bontha, Jun Liu

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For: MESOPOROUS-SILICA FILMS, FIBERS AND POWDERS BY EVAPORATION

Assistant Commissioner for Patents
Washington, D.C. 20231

DECLARATION OF DR. LIU
UNDER 37 CFR § 1.132

1. I am a Senior Staff Scientist (highest technical rank) at Battelle Memorial Institute (BMI), assignee of the above Bruinsma reissue patent application, and am one of the co-inventors of the invention described and claimed therein. My responsibilities include principal investigator and program manager for a wide range of programs for the Department of Energy, including one program related to the fundamental interactions between surfactants and metal oxide precursors in aqueous solutions. I have been a staff scientist with BMI for more than seven years.

2. My education includes a baccalaureate degree in Chemical Engineering from Hunan University and post-graduate degrees, including a Masters of Science in Ceramic Engineering and a PhD. in Materials Science from University of Washington. I have received the R&D 100 Award, Basic Energy Science Materials Science Award for Materials Chemistry: Significant Implication for DOE-Related Technologies, Best Paper Award of the American Ceramic Society, and Finalist for the Discover Magazine Award for Technology Innovation.

3. Previous work experience includes research assistant professor and research scientist at University of Washington from June 1990 to September 1992. My responsibilities included

performing research in ceramic synthesis, managing the Electron Microscopy Center, training students and faculties, and teaching electron microscopy.

4. I am a member of American Ceramic Society, American Chemical Society, and the Materials Research Society since 1990. I have published the following technical articles of interest in reputable professional journals, including Science, in connection with U.S. Patent No. 5,922,299 to Bruinsma et al. (hereinafter, the Bruinsma patent) (many of this articles are invited review articles, invited feature articles, or cover stories):

(1) J. Liu, M. Sarikaya, W. Y. Shih, W.-H. Shih and I. A. Aksay, "Role of Aggregation in the Formation of Colloidal Gold Particles," in Fractal Aspects of Materials, Vol EA-20, edited by J. H.Kaufmann, J. E. Martin and P. W. Schmidt, (Materials Research Society, Pittsburgh, Pennsylvania, 1989), pp. 147-50.

(2) J. Liu, W. Y. Shih, M. Sarikaya, I. A. Aksay, "Fractal Colloidal Aggregates with Finite Interactions," *Physical Review A*, 41 (4), 3206-13 (1990).

(3) J. Liu, W. Y. Shih, R. Kikuchi, I. A. Aksay, "Clustering of Binary Colloidal Systems: Theory," *Journal of Colloidal and Interface Science*, 142 (2), 357-68 (1991).

(4) W. Y. Shih, J. Liu, W.-H. Shih, and I. A. Aksay, "Aggregation of Colloidal Particles with a Finite Interparticle Attraction Energy," *Journal of Statistical Physics*, 62 (5/6), 961-84 (1991).

(5) B. C. Bunker, P. C. Rieke, B. J. Tarasevich, A. A. Campbell, G. E. Fryxell, G. L. Graff, L. Song, J. Liu, J. W. Virden, "Ceramic Thin Film Formation on Functionalist Interfaces Through Biomimetic Processing," *Science*, 261, 1286 (1993).

(6) P. C. Rieke, B. D. Marsh, L. L. Wood, B. J. Tarasevich, J. Liu, L. Song, and G. E. Fryxell, "Aqueous Solution Deposition Kinetics of Iron Oxyhydroxide on Sulfonic Acid Terminated Self-Assembly Monolayers," *Langmuir*, 11, 318-26 (1994).

(7) J. Liu, A. Y. Kim, J. W. Virden, and B. C. Bunker, "Effect of Colloidal Particles on the Formation of Ordered Mesoporous Materials," *Langmuir*, 11, 689-692 (1995).

(8) J. Liu, A. Y. Kim, J. W. Virden,a nd B. C. Bunker, "Heterogeneous Nucleation of Ordered Mesoporous Materials," in Advances in Porous Materials, edited by S. Komarneni, D. M. Smith, and J. S. Beck (Materials Research Society, Pittsburgh, Pennsylvania) 105 110 (1995).

(9) A. Y. Kim, J. Liu, J. W. Virden, and B. C. Bunker, "Non-Aqueous Synthesis of Multicomponent Mesoporous Materials," in Advances in Porous Materials, edited by S. Komarneni, D. M. Smith, and J. S. Beck (Materials Research Society, Pittsburgh, Pennsylvania) 111-116 (1995).

(10) H. Li, J. G. Darab, D. W. Matson, P. A. Smith, P. Hrma, Y. Chen, and J. Liu, "Phosphate-Sulfate Interaction in Simulated Low-Level Nuclear Waste Glasses," MRS Proceedings, (1996).

(11) B. J. Tarasevich, P. C. Rieke, and J. Liu, "Nucleation and Growth of Oriented Films onto Organic Interfaces," *Chemistry of Materials*, 8, 292-300 (1996).

(12) J. Liu, A. Y. Kim, and J. Virden, " Preparation of Mesoporous Spherulite in Surfactant Solutions," *J. Porous Materials*, 2, 201-205 (1996).

(13) B. J. Palmer and J. Liu, "Simulation of Self-Assembly in Surfactant Solutions," *Langmuir*, 12, 746-753 (1996).

(14) L. Q. Wang, J. Liu, G. J. Exarhos, and B. C. Bunker, "Investigation of Structure and Dynamics Surfactant Molecules in the Mesophase Silicates Using Solid-State 13C NMR," *Langmuir*, 12, 2663-2669 (1996).

(15) B. J. Palmer and J. Liu, "Effects of Solute-Surfactant Interactions on Micelle Formations in Surfactant Solutions," 12, 6015-6021, *Langmuir* (1996).

(16) J. Liu, A. Y. Kim, L. Q. Wang, B. J. Palmer, Y. L. Chen, P. Bruinsma, B. C. Bunker, G. J. Exarhos, G. L. Graff, P. C. Rieke, G. E. Fryxell, J. W. Virden, B. J. Tarasevich, L. A. Chick, "Self-Assembly in Materials Synthesis," *invited review* article, *Advances in Colloidal and Interface Science*, 69, 131-180 (1996).

(17) A. Y. Kim, B. Bruinsma, Li-Qiong Wang and J. Liu, "Amphoteric Route for Mesoporous Zirconia", *J. Chem. Soc. Chem. Commun.*, 161 (1997).

(18) X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, and J. Liu, K. M. Kemner, "Functionalized Monolayers on Ordered Mesoporous Supports (FAMMS)," *Science*, 276, 913, 1997.

(19) P. Liu, J. Liu, and A. Sayari, "Preparation of Porous Hafnium Oxide in the Presence of a Cationc Surfactant," *Chem. Commun.*, 577-572, 1997.

(20) P. Liu, I. L. Moudrakovski, J. Liu, and A. Sayari, "Mesostructured Vanadium Oxide Containing Dodecylamine," *Chm. Mater.*, 2511, 1997.

(21) J. Liu, L.-Q. Wang, W. D. Samuels and G. J. Exarhos, "Aggregation and Dispersion of Colloidal Suspensions by Inorganic Surfactants: Effect of Chemical Speciation and Molecular Conformation," *J. Physical Chemistry*, 101, 8264-8269, 1997.

(22) J. Liu, X. Feng, G. E. Fryxell, L- Q. Wang, A. Y. Kim, M. Gong, "Hybrid Mesoporous Materials with Functionalized Monolayers," *Advanced Materials*, 10, 161-165, 1998.

(23) J. Liu, X. Feng, G. E. Fryxell, L- Q. Wang, A. Y. Kim, M. Gong, "Hybrid Mesoporous Materials with Functionalized Monolayers," *Chemical and Engineering Technology*, 21, 96, 100, 1998.

(24) S. Baskaran, L. Song, J. Liu, Y. L. Chen, and G. L. Graff, "Titanium Oxide Thin Films on Organic Interfaces Through Biomimetic Processing," *J. Amer. Ceram. Soc.*, 81, 401 408, 1998.

(25) P. J. Bruinsma, A. Y. Kim, J. Liu, S. Baskaran, "Mesoporous Fibers by Rapid Evaporation," *Chem. Mater*, 9, 2507, 1998.

(25) S. Elder, Y. Gao, X. Li, J. Liu, D. E. McCready, C. F. Windisch, Jr, Chemistry of Materials, "Zirconia-Stablized 25 Å Anatase Crystallites in a Mesoporous Structure, " *Chem. Materials*, 10, 3140-3145, 1998.

(26) L. Q. Wang, G. J. Exarhos, and J. Liu, "NMR Magnetic Resonance -Characetrization of Self-Assembled Nanostructural Materials," *invited review*, *Advanced Materials*, 11, 1331-1341, 1999.

(27) X. Feng, L. Rao, T. R. Mohs, J. Xu, Y. Xia, G. E. Fryxell, J. Liu, and K. N. Raymond, "Self-assembled Monolayers on Mesoporous Silica, a Super Sponge for Actinides" Ceramic Transactions, Vol. 93, Environmental Issues and Waste Management Technologies IV, edited by J. C. Mara and G. T. Chandler, pp. 35-42, 1999. (Best Paper Award).

(28) G. E. Fryxell, J. Liu, T. A. Hauser, Z. Nie, K. F. Ferris, "Design and Synthesis of Selective Mesoporous Anion Traps," *Chem. Mater.*, 8. 2148-2154, 1999.

(29) S. Mattigod, G. E. Frxell, X. Feng, J. Liu, "Self-Assembled Monolayers on mesoporus Supports for Metal Separation," *invited*, in "Metal separation Technologies Beyond 2000," edited by. K. C. Liddell, D. J. Chaiko, TMS, Warrendale, Pennsylvania, 35-43, 1999.

(30) G. E. Fryxell, and J. Liu, "Design Surface Chemistry in Meosporous Silica," *invited review*, in Adsorption on Silica Surfaces, edited by E. Papirer, Marcel Dekker, Inc., 665-687, 2000,

(31) S. Choi, Y. Wang, Z. Nie, J. Liu, and C. H. F. Peden, "Mesoporous Silica Supported Acid Catalysts," *Studies in Surface Science and Catalysis,* edited by A. Corma, F. V. Melo, S Mendioroz and J. L. G. Fierro, Elsevier Science B. V., 965-970, 2000.

(32) K. M. Kemner, X. Feng, J. Liu, G. E. Fryxell, L. Q. Wang, A. Y. Kim, M. Gong, and S. Mattigod , "Investigation of the local chemical interactions between Hg and self-assembled monolayers on mesoporous supports" *J. Synchotron Rad.* 1999, 6, 633-635.

(33) J. Liu, G. J. Lumetta, J. W. Virden, G. L. Graff, N. G. Colton, B. C. Bunker, J. L. Krumhansl, "Characterization of Colloidal Phases in Tank Wastes," Proceedings of American Ceramic Society, 1999.

(34) G. E. Fryxell, J. Liu, S. Mattigod, "Self-Assembled Monolayers on Mesoporous Supports (SAMMS)-an Innovative Environmental Sorbent," *Materials Technology*, 14, 4, 183-193, 1999

(35) Y. Shin, T. S. Zemanian, G. E. Fryxell, L.-Q. Wang, and J. Liu, "Supercritical Processing of Functionalized Size Selective Microporous Materials," *Microporous and Mesoporous Materials*, 49-56, 2000.

(36) J. Liu, G. E Fryxell, S. Mattigod, T. S. Zemanian, Y. Shin, and L.-Q. Wang, "Synthesis and Applications of Functionalized Nanoporous Materials for Specific Adsorption," invited panel article for "Studies in Surface Science and Catalysis," edited by A. Sayari et al. Elsevier Science B.V., 929-738, 2000.

(37) J. Liu, G. E. Fryxell, M. Qian, L. -Q. Wang, Y. Wang, "Interfacial Chemistry in Self-Assembled Nanoscale Materials with Structural Ordered," *invited article, Pure and Applied Chemistry*, 72, 269-279, 2000.

(38) S. Baskaran, J. Liu, K. Domansky, N. Kohler, X. Li, C. Coyle, G. E. Fryxell, S. Thevuthasan and R. W. Williford, "Low Dielectric Constant Mesoporous Silica Films through Molecularly Templated Synthesis," *Advanced Materials*, 12, 291, 2000.

(39) L.-Q. Wang, J. Liu, G. J. Exarhos, K. Y. Flanigan, and R. Bordia, "Conformational Heterogeneity of Surfactant Molecules in Intercalated Clay Minerals Studied by Solid-State NMR," *J. Physical Chem., 104, 2810-2816,* 2000.

(40) G. E. Fryxell, J. Liu, S.V. Mattigod, L.Q. Wang, M. Gong, T.A. Hauser, Yuehe Lin and K. F. Ferris, and X. Feng, "Environmental Applications of Interfacially Modified Mesoporous Ceramics"; Ceramics Transactions, Volume 94, Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries, 2000.

(41) J. Liu, Y. Shin, G. E. Fryxell, L. Q. Wang, Zimin Nie, Jeong Ho Chang, Glen E. Fryxell, William D. Samuels, G. J. Exarhos, "Molecular Assembly in Ordered Mesoporosity: A New Class of Highly Functional Nanoscale Materials," invited feature article, *J. Phy. Chem. A. 104,* 8328-8339, 2000.

(43) Y. Shin, J. Liu, L.-Q. Wang, Z. Nie, W. D. Samuels, G. E. Fryxell, G. J. Exarhos, "Ordered Hierarchical Porous Materials: Towards Tunable Size-and-Shape Selective

Microcavities in Nanoporous in Nanopoorus Channel," hot paper, *Angewandte Chemie International Edition*, 39, 2702-2707, 2000.

(44) S. Thevuthasan, S. Baskaran, K. Domansky, J. Liu and M. Engelhard "Effectiveness of High Energy Ion beam Techniques for the Characterization of Mesoporous Low Dielectric-Constant Materials," accepted by *Nuclear Instruments and Methods in Physics Research - Section B*, 2000.

(45) J. Liu, G. L. Graff, G. E. Fryxell, S. Baskaran, J. W. Virden, P. Rieke, A. Campbell, G. McVay, M. Thompson, Y. Wang and C. Peden, "Molecularly Organized Nanocomposites and Their Applications," *invited review*, to be published in Nanophase and Nanostructured Materials, edited by Z.L. Wang, Y. Liu and Z. Zhang.

5. I have thoroughly studied and understand the Bruinsma patent and the patents and technical publications cited in the Background section thereof. I also have a working knowledge of the field of surfactant chemistry and the use of surfactants as templates to make mesoporous films and powders.

6. I have thoroughly studied and understand U.S. Patent No. 5,858,457 to Brinker, et al. (hereinafter the Brinker patent) and the patents and technical publications cited in the Background section thereof.

7. I am an expert in the field of surfactant chemistry and mesoporous materials. I have given invited seminars and plenary lectures in numerous international and national conferences and workshops, and in many major universities in the area of surfactant templated mesoporous materials. My work in this area has been widely reported and featured by Scientific American, Popular Science, Discover, Business Week, Popular Mechanics, and many other newspapers and magazines.

8. The term "critical micelle concentration (CMC)" as it appears in the Brinker patent refers to a threshold surfactant concentration beyond which the addition of new surfactant to the solution favors the formation of micelles (micelles are aggregated clusters of surfactant molecules), instead of free surfactant molecules. (See, for example, J. Israelachvili, Intermolecular & Surface Forces, Academic Press, San Diego p.351 (1992), attached hereto as Exhibit A.) This term of art would have been known by one of ordinary skill in the art at the application filing date of the Bruinsma patent, or August 26, 1997. At the CMC, several thermodynamic

properties, such as conductivity, surface tension, turbidity, and osmotic pressure go through a discontinuous transition. I and my colleague Dr. Liang Liang, a research scientist with BMI working under my supervision, have replicated experiments in Example 1 of the Bruinsma Patent in order to confirm that the precursor solution used in the original experiments inherently included micelle concentrations much less than the critical micelle concentration to which Brinker alludes.

9. I and Dr. Liang Liang replicated the experiments by carefully replicating and controlling the conditions, the chemicals, the process steps, and the CTAC/TEOS mole ratios described in the reissue application with a molar ratio for TEOS:H2O:HCl:EtOH of 1.0:7.2:0.1:5.7 that was used in Example 1 to generate Figure 2 in the Bruinsma patent. The surfactant concentration was varied to cover all the data points in Figure 2. We then determined the CMC, by measuring the conductivity of the solution as a function of the surfactant concentration, as would have one of ordinary skill in the art who had read the Brinker patent and its claims containing that term. The CMC for the solutions used in Example 1 for Figure 2 were determined to be about 0.21 mol/liter. This value translates to a CTAC/TEOS ratio of about 0.16. I have shown the position of the CMC on the graph of Fig. 2 of the Bruinsma patent, attached hereto as Exhibit B. It may be seen from this plot that the surfactant concentrations of many of the experimental results (i.e., those having a CTAC/TEOS MOLE RATIO of less than approximately 0.16), are below the CMC and a few are above the CMC. Of those results below the critical micelle concentration, it is my belief that at least three (i.e., those having a CTAC/TEOS MOLE RATIO of less than approximately 0.10) are "much less than" the CMC, as Brinker used that term, for example, in claim 1. I believe that because of the definition of CMC, one of ordinary skill would have concluded that "much less than" would include surfactant concentrations representing less than a substantial fraction of the CMC (i.e. surfactant concentrations sufficiently below the CMC to provide a margin of error not to exceed the CMC), certainly those that are less than a CTAC/TEOS ratio of 0.1 in Figure 2.

10. In a brief summary, it is my expert opinion that a micelle concentration much less than a CMC would have been concluded by a person of ordinary skill in the pertinent art on August 26,

1997 to be an inherent characteristic of at least some of the precursor solutions described and illustrated in the Bruinsma patent.

11. I, the undersigned, declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated this 7th day of November, 2000.

Jun Liu
Senior Staff Scientist (Grade VI)
of Battelle Memorial Institute, Richland, WA